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VII. "On Supersaturated Saline Solutions."—Part II. By
CHARLES TOMLINSON, F.R.S. Received May 17, 1870.

(Abstract.)

The object of this paper is to develop more fully the principles attempted to be established in Part I.* not only by clearer definitions of terms, but also by new facts and conclusions. The paper is divided into two sections; in the first of which are stated the conditions under which nuclei act in separating salt or gas or vapour from their supersaturated solutions, while in the second section is shown the action of low temperatures on supersaturated saline solutions.

The first section opens with definitions of the terms used.

A *nucleus* is a body that has a stronger attraction for the gas or vapour or salt of a solution than for the liquid that holds it in solution.

A body is *chemically clean* the surface of which is entirely free from any substance foreign to its own composition. Oils and other liquids are chemically clean if chemically pure, and contain no substance, mixed or dissolved, that is foreign to their composition. But with respect to the nuclear action of oils &c., the behaviour is different when such bodies exist in the mass, such as a lens or globule, as compared with the same bodies in the form of films.

Catharization is the act of clearing the surface of bodies from all alien matter, and the substance is said to be *catharized* when its surface is so cleared.

As everything exposed to the air or to the touch takes more or less a deposit or film of foreign matter, substances are classed as *catharized* or *uncatharized* according as they have or have not been so freed from foreign matter.

Referring to the definition of a nucleus, substances are divided into *nuclear* or *non-nuclear*.

The nuclear are those that may, *per se*, become nuclei. The non-nuclear are those that have not that quality.

The nuclear substances would seem to be comparatively few, the larger number of natural substances ranking under the other division.

Under nuclear substances are those vapours and oily and other liquids that form thin films on the surfaces of liquids and solids; and generally all substances in the form of films, and only in that form. Thus a stick of tallow, chemically clean, will not act, but a film of it will act powerfully; and again, a globule of castor-oil will not act, if chemically clean; but in the form of a film, whether chemically clean or not, it will act powerfully.

If a drop of a liquid be placed on the surface of another liquid it will do one of three things (apart from chemical action),—(1) it will diffuse through the liquid, and in general, under such circumstances, not act as a

* Proc. Roy. Soc. vol. xvi. p. 403; Phil. Trans. 1868, p. 659.

nucleus ; or (2) it will spread out into a film, or (3) remain in a lenticular shape. It becomes a film or a lens according to the general proposition, that if on the surface of the liquid A, whose surface-tension is a , we deposit a drop of the liquid B, whose surface-tension, b , is less than a , the drop will spread into a film ; but if, on the contrary, b be greater than a , or only a little less, the drop will remain in the form of a lens. Hence if B spread on A, A will not spread on the surface of B.

This general proposition may not always apply in the case of supersaturated saline solutions, on account of the *superficial viscosity*, or the greater or less difficulty of the superficial molecules to be displaced.

A glass rod drawn through the hand becomes covered with a thin film, or the same rod by exposure to the air contracts a film by the condensation of floating vapours, dust, &c., and in either case is brought into the nuclear condition.

A second class of nuclear bodies are permanently *porous* substances, such as charcoal, coke, pumice, &c. The action of these is chiefly confined to vaporous solutions, and if catharized having no power of separating salts from their supersaturated solutions.

Under the non-nuclear, forming by far the larger class of substances, are glass, the metals, &c., while their surfaces are chemically clean.

Among the non-nuclear substances will be found air ; for its ascribed nuclear character is due, not to itself, but to the nuclear particles of which it is the vehicle. Thus, as stated in Part I., if air be filtered through cotton-wool it loses its apparent nuclear character ; so also if heated.

When a catharized body is placed in a supersaturated solution, such solution, as explained in Part I., adheres to it as a whole ; but if such body be non-catharized, the gas or vapour or salt of the solution adheres to it more strongly than the liquid portion, and hence there is a separation. In the present paper it is shown that an active or non-catharized surface is one contaminated with a film of foreign matter, which filmy condition is necessary to that close adhesion which brings about the nuclear action ; for it can be shown that an oil, for example, is non-nuclear in the form of a lens or globule, but powerfully nuclear in the form of a film.

Some liquids (absolute alcohol for example) form films, and act as nuclei by separating water instead of salt from supersaturated solutions.

Other liquids (glycerin for example) diffuse through the solutions without acting as nuclei.

Fatty oils may slowly saponify, or oil of bitter almonds form benzoic acid in contact with supersaturated solutions of Glauber's salt without acting as nuclei.

The solutions (say of Glauber's salt) are prepared with 1, 2, or 3 parts of the salt to 1 part of water ; they are boiled, filtered into clean flasks, and covered with watch-glasses. When cold, the watch-glass being lifted off, a drop of oil is deposited on the surface of the supersatu-

rated solution. In an experiment described, a drop of pale seal-oil formed a well-shaped film, with a display of iridescent rings, and immediately from the lower surface of the film there fell large flat prisms with dihedral summits of the 10-atom sodic sulphate. The prisms were an inch or an inch and a half in length, and three-eighths of an inch across. The crystallization proceeded from every part of the lower surface of the film, and as one set of crystals fell off, another set was formed, until the whole solution became a mass of fine crystals in a small quantity of liquid, an effect quite different from the usual crystallization which takes place when a supersaturated solution of Glauber's salt is subjected to the action of a nucleus at one or two points in its surface, as when motes of dust enter from the air, or the surface is touched with a nuclear point. In such case small crystalline needles diverge from the point and proceed rapidly in well-packed lines to the bottom, the whole being too crowded and too rapid to allow of the formation of regular crystals.

Similar experiments were made on solutions of Glauber's salt of different strengths, with drops of ether, absolute alcohol, naphtha, benzole, the oils of turpentine, cajuput, and other volatile oils, sperm, herring, olive, linseed, castor, and other fixed oils of animal and vegetable origin, with this general result, that whenever the liquid drop spread out into a film, it acted as a powerful nucleus; but when the oil formed a lens there was no separation of salt, even when the flasks were shaken so as to break up the lens into small globules. If, however, a sudden jerk were given to the flask so as to flatten some of the globules against its sides into films, the whole solution instantly became solid. A similar effect was produced by introducing a clean inactive solid for the purpose of flattening a portion of oil against the side of the flask.

Stearine from sheep's tallow that had been exposed to the air produced immediate crystallization, but by boiling the solution and covering the flasks, the stearine, now catharized, had lost its nuclear character on the cold solution. Similar observations were made with the fixed oils that form lenses or globules in the solution. So also volatile oils containing products of oxidation, dust, &c. are nuclear, but when catharized by being redistilled they are inactive in the globular state, active in the form of films.

Supersaturated solutions of potash alum, ammonia alum, sodic acetate, and magnesia sulphate were also operated on with results similar to those obtained with solutions of Glauber's salt.

When a liquid forms a film on the surface of a supersaturated solution, the surface-tension of the solution is so far diminished as to bring the film into contact with the solution, when that differential kind of action takes place whereby the salt of the solution adhering more strongly to the film than the water of the solution, the action of separation and crystallization, thus once begun, is propagated throughout. A similar action takes place with solid bodies that have contracted filmy nuclei by being touched or drawn through the hand, or merely exposed to the air;

they are active or nuclear by virtue of the films of matter which more or less cover them.

On the other hand, when a drop of oil (or many drops) is placed on the surface of a supersaturated saline solution, and it assumes the lenticular form, or even flattens into a disk, such lens or disk is separated from actual contact with the solution by surface-tension. That the adhesion is very different from that of a film may be shown by pouring a quantity of recently distilled turpentine, for example, on the surface of chemically clean water, and scraping upon it some fragments of camphor; these will be immediately covered with a solution of camphor in the oil, which solution will form iridescent films, and sail about with the camphor, vigorously displacing the turpentine, and cutting it up into smaller disks and lenses. So in the case of supersaturated saline solutions, the oil-lens is not sufficiently in contact with the surface of the solution to allow of the exertion of that differential kind of action whereby salt is separated. Even when, by shaking, the oil is broken up into globules, and these are submerged, they are still so far separated from the solution by surface-tension as to prevent actual contact.

In the second section it is shown that solutions of certain salts which remain liquid and supersaturated at and about the freezing-point of water, by a further reduction in temperature, to from 0° Fahr. to -10° and in the absence of a nucleus, rather solidify than crystallize, but on being restored to 32° recover their liquid state without any separation of salt.

A solution of ferrous sulphate, for example, at 0° Fahr. formed tetrahedral crystals at the surface, which spread downwards until the contents of the tube became solid. In snow-water at 32° the frozen mass shrank from the sides of the tube, formed into a smooth rounded mass, and gradually melted, leaving the solution clear and bright without any deposit. On removing the cotton-wool from the mouth of the tube, small but well-shaped rhomboidal crystals soon filled the solution.

A similar experiment was tried with the double salt formed by mixing in atomic proportions solutions of the zincic and magnesic sulphates. A supersaturated solution of this salt at about -8° Fahr. became solid, and it melted quickly at 32° . Such a solution may be solidified and melted a number of times, provided it be protected from the action of nuclei; but if the cotton-wool be removed from the tube, even when the contents are solid, and be immediately reinserted, there will be a separation of the salt during the melting, in consequence of the entrance of nuclear particles from the air.

Solutions of such a strength as to be only saturated at ordinary temperatures, and therefore not sensitive to the action of nuclei, become very much so by reduction of temperature below 32° Fahr. Salts that contain a large amount of water of crystallization, such as the zincic and magnesic sulphates, require only a small portion of added water in order

to form supersaturated solutions, and they become more sensitive to the action of nuclei as the temperature falls, or, in other words, as they become more highly supersaturated. Thus a very strong solution of calcic chloride, which is not sensitive to nuclei at 40° or 45°, becomes very much so at 24° to 34°.

The sodio-zincic sulphate contains only 4 proportionals of water of crystallization, and hence its supersaturated solutions are not stable at low temperatures. When freshly made, they may be reduced to 10° Fahr. without separation of the salt; but by repose, even in clean tubes and in the absence of nuclei, long crystals of the separated salts occupy the length of the tube, but they are invisible on account of having the same refractive index as that of the solution in which they are immersed. In the course of time, probably from the escape of vapour of water through the porous plug, they become visible.

A solution of the ammonia zincic sulphate at 4° Fahr. formed beautiful large feathery crystals of an opaque white, which gradually filled the tube. They melted rapidly at 32°.

A supersaturated solution of nickel sulphate resisted a temperature of 6° Fahr. Mixed with an equivalent weight of cupric sulphate, the two salts separate if the solution be exposed to the air, but in closed tubes the solution at 0° Fahr. forms beautiful feathery crystals, which melt rapidly at 32°, without any separation of salt.

Similar phenomena are produced by a supersaturated solution of zinc sulphate and potash alum in equivalent proportions exposed to a temperature of 4° Fahr. A similar solution of the cupric and magnesic sulphates at —4° also became solid, and melted rapidly at 32°.

Experiments were also made with the sodic and magnesic sulphates, cadmic, and some other sulphates. The addition of potassic sulphate to other sulphates, in atomic proportions, forms double salts, which, so far as they were examined, do not form supersaturated solutions.

The effect of low temperatures was in some cases to throw down a portion of the salts in the anhydrous form, upon which were formed by repose crystals of a lower degree of hydration than the normal salt. Some cases of this kind are described in the paper.

VIII. "On Furfur'aniline and Furfurtoluidine." By JOHN STENHOUSE, LL.D., F.R.S. Received May 19, 1870.

In an epistolary communication to Mr. H. Watts * I stated that "The most abundant and economical source of furfrol is in the preparation of garancin by boiling madder with sulphuric acid. If the wooden boilers, in which garancin is usually manufactured were fitted with condensers, furfrol might be obtained in any quantity without expense. Furfrol is

* Watts's Dictionary, ii. 751.